

## STEAM PRETREATMENT FOR COAL LIQUEFACTION

O. Ivanenko, R.A. Graff, V. Balogh-Nair, C. Brathwaite  
Departments of Chemical Engineering and Chemistry  
The City College of New York, New York, NY, 10031

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### INTRODUCTION

Development of commercially viable and environmentally sound processes for coal liquefaction remains a formidable challenge. Although advances in coal liquefaction technology in recent years have led to the production of liquids of improved quality, this improvement has been achieved mainly by increased consumption of expensive catalyst. Catalyst and capital equipment costs are major factors in the high price of the coal-derived liquids.

One way to improve the economics of direct liquefaction is to modify the coal feed before solubilization. A variety of physical and chemical methods of coal treatment prior to low severity liquefaction have been found to significantly improve yield and quality of the product, making it superior to those obtained at high severity conditions. Many studies have shown that treatments such as alkylation, acylation, partial oxidation and alkali hydrolysis weaken and rupture the cross-linked bonds and result in a partially depolymerized coal. Although all of these methods of enhancing coal reactivity somewhat improve liquefaction yield, none has yet been employed as a process step in liquefaction. Chemical treatment methods remain in the laboratory mainly because they employ expensive and sometimes hazardous reagents.

The work described here is based on the use of steam as a pretreatment agent in noncatalytic coal-donor solvent liquefaction. Advantages of this approach are that steam is among the cheapest of reagents and does not incorporate undesired chemical residues into the coal structure.

Studies have already demonstrated the effectiveness of exposing Illinois No.6 coal to subcritical steam in the temperature range 320-360°C at 50 atm as a pretreatment for room temperature pyridine extraction and for flash pyrolysis (Graff and Brandes, 1987). It was observed that the pyridine extraction yield from steam treated coal gradually increases and reaches a maximum at a pretreatment temperature of 340-350°C. At temperatures above 370°C the effect is extinguished. Yield of liquids in coal pyrolysis was more than doubled and the total volatiles yield was increased by about 20%. When steam treated coal was exposed to ambient air, both pyrolysis and extraction yields were reduced to the level of raw coal. Analysis of pyrolysis liquids from pretreated Illinois No.6 coal showed a decrease in molecular weight with a simultaneous increase in oxygen content compared to raw coal (Graff *et al.*, 1988). Based on the results of analyses performed on raw and steam pretreated coal (Brandes *et al.*, 1989) it was concluded that during steam pretreatment new hydroxyl groups are introduced. As a result, the covalent cross-links in coal are greatly reduced yielding a partially depolymerized coal, potentially, an improved feedstock for liquefaction processes.

With this success of steam pretreatment in pyrolysis, it was logical to test its application to direct liquefaction. Previous attempts by others to obtain an improvement in liquefaction yield by this method had, however, failed. As noted above, pyrolysis studies showed that heating coal above 360°C could destroy the effect of pretreatment. It was, therefore, reasoned that the heating of pretreated coal to liquefaction temperatures must be done rapidly to minimize deleterious retrogressive reactions. A tubing bomb or stirred autoclave (employed in the conventional way) would not be adequate to carry out liquefaction under rapid heating conditions. One way to achieve high heating rates is to use a method in which a slurry of pretreated coal is injected into a hot liquefaction reaction vessel (Whitehurst *et al.* 1976). A system of this type, with some modifications, was designed, assembled, tested and used for the liquefaction tests. Furthermore, as it is known that the benefits of pretreatment are observed only if exposure of steam treated coal to air is rigorously avoided, it is necessary to conduct all operations with pretreated coal under an inert atmosphere. To satisfy this requirement, a nitrogen filled glove bag is used for sample workup and the oxygen concentration of the bag monitored by mass-spectrometer. To verify successful pretreatment, the pyridine extraction yield is determined for each steam treated coal sample.

In this work liquefaction tests of raw and steam pretreated Illinois No. 6 coal were made to determine the pretreatment effect on yield of liquids and on quality of product. These tests were conducted using the slurry injection autoclave described above pressurized with hydrogen and using tetralin as the donor solvent. The effect of exposure of treated coal to air and the role

of coal slurry heating rate were examined at three different conditions of liquefaction severity.

## EXPERIMENTAL METHODS

**Coal Sample.** Pretreatment and liquefaction experiments were conducted with Illinois No.6 coal from the Pennsylvania State University Sample Bank (DECS-2) ground under nitrogen to pass 200 mesh using a gas impact pulverizer (Trost). Ground coal was riffled, placed in a glass jars, flushed with inert gas, sealed, and stored under refrigeration.

**Steam Pretreatment.** Steam pretreatment was conducted in a continuous flow of steam using the procedure described by Graff and Brandes (1987) and Graff *et al.* (1988, pp 3-5). The coal was reacted with 50 atm steam at 340°C for 15 minutes (optimum pretreatment conditions for Illinois No.6 coal).

**Liquefaction.** Liquefaction experiments were conducted with raw coal, steam treated coal and steam treated coal exposed to air under conditions of both rapid and slow heating, using tetralin as a hydrogen donor solvent. The liquefaction apparatus (Figure 1) consists of a 300 ml stirred autoclave (Autoclave Engineers EZE-Seal, model #P-419) and coal slurry injection system (loading reservoir and 1000 psia rupture disc assembly which separates the reservoir from the autoclave). Nitrogen and hydrogen are supplied from high pressure cylinders.

Rapid heating liquefaction is conducted as follows:

Sixty grams of deoxygenated tetralin are placed into the reaction vessel and the autoclave is sealed. After the system is leak tested with nitrogen at 2000 psia with the bypass line valve open, the reactor is flushed with hydrogen at atmospheric pressure and then heated using an electric furnace and keeping the bypass line valve closed. While the reactor is heated, slurry is prepared in a nitrogen filled glove bag from the pretreated coal and the solvent. The slurry is made of 1/3 part of coal and 2/3 parts of solvent using about 20 grams of coal. When the autoclave has been preheated to operating temperature, two syringes are filled, one with about 40 ml of slurry and one with 20 ml of solvent. The syringes are attached to the loading line, the loading valve is opened, and the slurry reservoir is sequentially filled with 10 ml of solvent, coal slurry (full contents of the syringe), and, finally, 10 ml of solvent. The loading valve is then sealed and hydrogen at the desired pressure is applied. This causes the rupture disc to burst, injecting slurry into the reactor and pressurizing the system. The valve above the reservoir is then closed. The reaction temperature is maintained with  $\pm 5^\circ\text{C}$  accuracy. The run duration is measured from coal injection. Then the heater is turned off, removed from the autoclave and the run is terminated.

In slow heating liquefaction tests the same procedure is employed except that slurry is injected when the autoclave is at room temperature. The reaction mixture is then heated to operating temperature. The reaction time count starts when the desired operating temperature is reached.

After the liquefaction run is completed and the reactor cooled down, coal conversion is determined using Soxhlet extraction as described by Joseph (1991). The liquid product is classified as hexane solubles (oils + gases), toluene solubles (asphaltenes), and THF solubles (preasphaltenes). In later runs, after cool down, vent gas from the autoclave is analyzed continuously sampling the gas vented from the autoclave directly into a mass spectrometer (Extranuclear Laboratories, Inc.; Model C50). The total gas yield, including volatiles loss during pretreatment (8 wt% at the conditions used), is determined and then subtracted from the value of hexane solubles (oil + gas) to obtain the yield of oils alone.

## RESULTS AND DISCUSSION

Liquefaction runs were conducted with Illinois No. 6 coal at three sets of conditions:

- High severity: 400°C, 1500 psia, 30 minutes,
- Low severity a: 350°C, 1500 psia, 30 minutes, and
- Low severity b: 385°C, 1500 psia, 15 minutes.

The results are shown in Tables 1, 2, and 3, classified according to the liquefaction conditions employed. All yields are based on the moisture and ash free (maf) raw coal charge.

**High Severity Liquefaction.** First, raw coal was examined under slow (run C2) and rapid (runs 2 and 8) heating liquefaction conditions. Then, a series of tests with steam treated coal were conducted: runs 6 and 12 were carried out under rapid heating conditions. The importance of preventing the exposure of pretreated coal to oxygen (run 11) and the importance of rapid heating (run 10) for the liquefaction were also demonstrated. Results are shown in Table 1.

The total yield of liquid product from raw coal obtained at rapid heating conditions appears to be slightly lower than at slow heating due to the longer overall reaction time in a slow heating run. The yield of oils, however, is increased and preasphaltene yield is decreased. No improvement in the yields was observed when steam pretreated coal was subjected to the liquefaction under slow heating. Compared to raw coal, a lower total yield as well as a lower yield of each fraction were obtained. In rapid heating liquefaction, however, the yield of hexane solubles are substantially increased while asphaltenes are reduced. When steam treated coal is deliberately exposed to ambient air for one hour before slurrying with deoxygenated tetralin, the pretreatment effect deteriorated. The oil yield decreased even below the value for raw coal with rapid heating. Total yield also decreased. Asphaltene yield is higher and preasphaltenes yield is lower when an exposure to air is prevented.

**Low Severity Liquefaction a.** Raw and steam pretreated coal were tested under rapid heating conditions at reduced severity (low severity liquefaction a). In addition to liquid product characterization, the amount of gas formed in the process was also determined. Liquefaction yields are shown in Table 2.

The results obtained under these reduced severity conditions show no improvement in the liquefaction yields between raw and steam pretreated coal. (That the pretreatments were successful was confirmed by the increased pyridine extraction yields.) Steam pretreatment did, however, increase gas yield at the expense of oils.

A possible explanation for the lack of improvement in yields after steam pretreatment may be found in the temperature history in the autoclave. The coal slurry (made of raw or steam treated coal) was injected into the autoclave preheated to 350°C. In all cases the injection caused the temperature to drop below 300°C. This was followed by a recovery to 350°C in about 1.5 minutes. Consequently, the sample had passed through a region below 360°C where retrogressive reactions occur, resulting in low yield of the liquid product and in a higher yield of gas. Perhaps, the chosen reaction temperature itself, 350°C, is where retrogressive reactions occur.

**Low Severity Liquefaction b.** To keep the reaction temperature higher after slurry injection and during the reaction, the low severity liquefaction temperature was increased to 385°C (which is above the upper limit of pretreatment), the reaction time reduced to 15 minutes, and the pressure was left unchanged at 1500 psia. The procedure was also slightly modified: the autoclave was initially preheated to 400°C. After the temperature drop caused by the slurry injection, the temperature was raised to 385°C. The results are shown in Table 3. In all rapid heating liquefaction experiments the reaction temperature never dropped below 320°C.

Low severity liquefaction b tests show a strong improvement in the quality of product resulting from steam pretreatment under rapid heating conditions (runs no. 31 and 34 compared to runs no. 32 and 33). The yields of hexane solubles were increased with a slight reduction in the total gas make. Remarkably, the oil yields are doubled while preasphaltenes are reduced. This improvement in the liquid quality occurred together with an increase in the total yield of liquids.

Exposure of steam treated coal to air (runs no. 35 and 36) resulted in a drop in the yield of hexane solubles and oils almost to the level of raw coal. The total yield of liquids also decreased. In slow heating liquefaction (runs no. 37 and 38), the total yield of liquids has dropped compared to rapid heating, but is still higher than raw coal under rapid heating. Of the three liquid fractions, only hexane solubles are distinctly affected by heating rate. Under slow heating conditions the highest total gas make was observed, the total yield of hexane solubles and oils alone have intermediate value between raw and steam treated coal under rapid heating. The higher total yield under slow heating liquefaction may result from a longer reaction time (it takes up to 30 minutes to preheat autoclave to 385°C), since the liquefaction process starts before the reactor temperature reaches 385°C, even under low pressure.

Summarizing these results, the behavior of Illinois No.6 coal in low severity b liquefaction follows the same trends as high severity. The best results, highest total yield and yield of hexane solubles, are obtained from steam pretreated coal under rapid heating conditions. Moreover, the improvement in the hexane solubles is achieved as a result of an increase in the yield of oils and a decrease in gas yield (at least at low severity). The liquefaction yields (total yield and hexane solubles) obtained from steam treated coal under slow heating conditions have intermediate values between raw and steam treated coal under rapid heating. When steam treated coal is deliberately exposed to air, the total yield drops to the level of raw coal (rapid heating), the yield of hexane solubles is slightly higher than from raw coal under rapid heating

but does not exceed the value obtained under slow heating.

## CONCLUSIONS

The following conclusions are drawn from this work:

1. Steam pretreatment substantially improves the quality of the liquid product in coal slurry liquefaction. Under low severity conditions, the oil yield is more than doubled, going from 12.5 to 29 wt %.
2. The benefits of steam pretreatment can be realized only if the pretreated coal is rapidly heated to liquefaction temperature. This is necessary in order that the pretreated coal pass quickly through the region of retrogressive reactions. This region, in which retrogressive reactions can mitigate or even destroy the effects of pretreatment, extends downward from 360°C to perhaps as low as 320°C. The upper limit on heating time can not yet be specified, but appears to be about one minute (which was the recovery time for the low severity b series of tests).
3. Pretreated coal must be protected from oxygen to preserve the benefits of pretreatment.

## ACKNOWLEDGMENT

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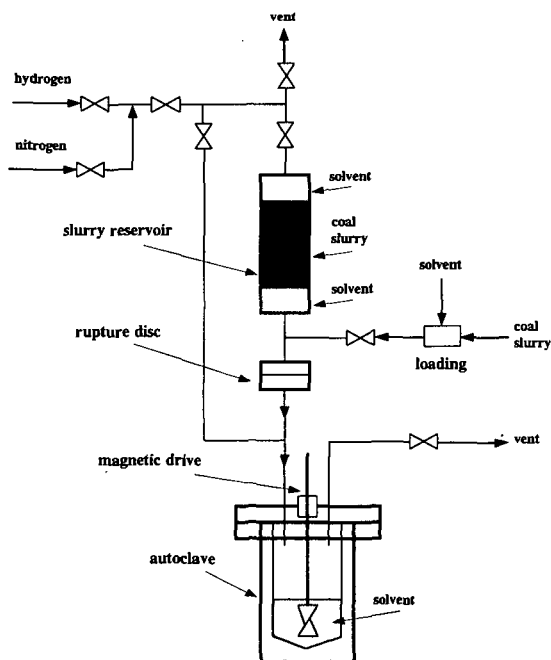


Figure 1. Stirred Autoclave with Coal Slurry Injection (Shown Prior to Coal Slurry Injection)

**Table 1.**  
**High Severity Liquefaction of Illinois No.6 coal.**  
**(400°C, 1500 psia, 30 minutes)**

Run No.	Conditions	Conversion (%wt)			
		Total (liquid + gas)	Hexane Solubles Oils + Gas	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
C2	raw coal slow heating	81.6	37.0	16.9	27.7
2	raw coal	73.8	42.2	10.0	21.6
8	rapid heating	80.0	48.7	16.7	14.6
10	steam treated coal slow heating	73.8	35.2	14.4	24.2
6	steam treated coal	85.7	60.1	17.2	8.4
12	rapid heating	79.3	55.8	14.7	8.8
11	steam treated coal, exposure to air, rapid heating	66.3	38.6	19.8	7.9

**Table 2.**  
**Low Severity a Rapid Heating Liquefaction of Illinois No.6 Coal.**  
**(350°C, 1500 psia, 30 min)**

Run No.	Conditions	Conversion (wt %)					
		Total (liquid + gas)	Total	Hexane Solubles Gas	Oils	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
28	raw coal	73.9	47.4	5.52	41.88	10.9	15.6
29	steam treated	71.3	47.1	13.52	33.58	9.5	14.7
30	coal	70.9	42.6	12.02	30.58	11.0	17.0

**Table 3.**  
**Low Severity b Liquefaction of Illinois No.6 Coal.**  
**(385°C, 1500 psia, 15 min)**

Run No.	Conditions	Conversion (% wt)					
		Total (liquid + gas)	Total	Hexane Solubles Gas	Oils	Toluene Solubles Asphaltenes	THF Solubles Preasphaltenes
32	raw coal	71.6	27.7	13.7	14.0	17.9	26.0
33	rapid heating	71.3	26.5	15.5	11.0	20.2	24.6
31	steam treated coal	71.3	41.8	11.9	29.9	16.4	19.3
34	rapid heating	70.9	38.9	10.3	28.6	15.8	21.5
35	steam treated coal,	71.3	30.5	14.9	15.6	18.9	23.3
36	exposure to air	70.9	31.2	13.8	17.4	17.1	23.1
37	steam treated coal	71.3	35.2	16.4	18.8	20.0	19.7
38	slow heating	70.9	34.1	19.2	14.9	18.6	27.2